

# Liquid Crystalline Polymorphism of Methyl and Ethyl *trans*-4-[[4'-(alkanoyloxy)phenyl]diazanyl]benzoates

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Authors present two new homologous series of liquid-crystalline compounds, methyl and ethyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates, synthesis and investigation of their mesogenic properties. In the methyl series only nematic phase was detected and in the ethyl series nematic and smectic mesophases. Influence of the alkyl chain length on the phase transition temperatures and their entropic values are discussed and compared with literature data.

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## 1. Introduction

Azobenzenes belong to the first identified on the properties liquid-crystalline molecules studied at the beginning of the twentieth century [1–3]. At that time primarily methyl and ethyl derivatives have been studied. Vorlaender began the study of whole homologous series in the 30's [4], but the biggest growth was observed 40 years later [5]. At the time there were discovered a lot of interesting properties of azobenzene. For example, light-sensitivity, that allowed further applications of these substances in the LCD industry.

In the early 90's azobenzenes became more popular. Control of isomerization process affects many physical properties. This contributed to the creation of a new branch of science, which is optoelectronics [6]. Today we see a very rapid development of optical applications, which desperately needs a variety of photorefractive materials, including those with additional ferroic or liquid-crystalline properties [7–9].

This paper presents two new series of liquid-crystalline compounds, which are derivatives of azobenzene. The first group (3a-n) consists of methyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates, while the second group (3b-n) of ethyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates. From 30 investigated in this paper compounds only five were described in literature [5] in 5 publications [10–14]. Ethyl 4-[[4-(methyloxy)phenyl]diazanyl]benzoate (3b-2) was the first compound described by Volreander's pupil Bergt in 1925 in his Ph.D. thesis [10]. The second paper by Knaak et al. [11] published in 1972 has a review character and among many presented nematic azobenzene derivatives. In this publication there were only republished Bergt's data. New results with four new compounds were described by Taiwan's group in series of three papers [12–14].

We critically compared these data with our results and presented in this paper. It is interesting that from the possible 210 alkyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates only 5 derivatives were described in literature. Our intention was to design mainly molecules with longer alkyl chains where we expected to find more interesting liquid-crystalline polymorphism.

## 2. Experimental

### 2.1. Measurements

NMR spectra in CDCl<sub>3</sub> were obtained by using Bruker Avance III 500 MHz high resolution NMR spectrometer. The percentage contents of the elements (EA) were measured by Vario EL III elemental analyzer. Differential scanning calorimetry (DSC) measurements were performed by Perkin Elmer 8500 calorimeter in nitrogen atmosphere. Heating and cooling curves have been recorded at the rate of 10 K min<sup>-1</sup>. Phase transitions and textures were observed by Olympus polarized light microscope BX61-P (TRF) equipped with Linkam hot stage and Motic digital camera. Phase transition temperatures were calculated from thermograms measured at the scan rate 10 K min<sup>-1</sup>.

### 2.2. Synthesis

Main root of synthesis is presented in Fig. 1.

#### 4-[[4-(4-Hydroxyphenyl)diazanyl]benzoic acid (1).

This synthesis was done according to the procedure described by Hillemann et al. [15]. 4-aminobenzoic acid (50 g, 0.365 mol) was dissolved in 1 M aqueous HCl and kept in the ice bath at 0–5 °C. NaNO<sub>2</sub> (27.5 g, 0.365 mol), dissolved in a minimum amount of water, was added dropwise to the solution and stirred for about 30 min. Sodium carbonate (53.0 g, 0.500 mol) and phenol (34.4 g, 0.365 mol) were dissolved in 200 ml water and then stirred for 3 h at 0–5 °C. The resulting mixture was next neutralized with diluted HCl and yellow crude product was received. It was filtered off and dried in the air. Yield: 79.5 g (90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.26 (d, 2H), 7.96 (dd, 4H), 7.21 (d, 2H).

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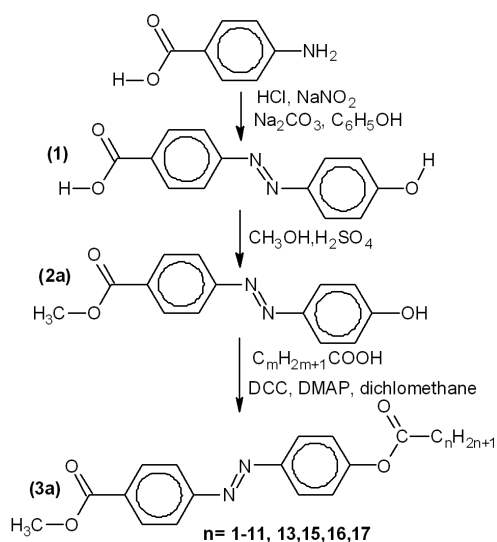


Fig. 1. Synthesis of alkyl 4-[[4-(alkanoyloxy)phenyl]diazenyl]benzoates.

*Methyl 4-[[4-(4-Hydroxyphenyl)diazenyl]benzoate (2a).*

Compound (1) (5 g, 20 mmol), 200 ml dry methanol and 1 ml concentrated sulfuric acid were refluxed overnight. The reaction mixture was then poured into cold water, received precipitate was filtered off and dried in air. Yield: 60% (3.1 g).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d, 2H), 7.94 (m, 4H), 7.10 (d, 2H), 3.84 (s, 3H).

*Ethyl 4-[[4-(4-Hydroxyphenyl)diazenyl]benzoate (2b).*

Compound (1) (5 g, 20 mmol), 200 ml dry ethanol and 1 ml concentrated sulfuric acid were refluxed overnight. The reaction mixture was then poured into cold water and the received precipitate was filtered off, and dried in air. Yield: 73% (3.9 g).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20 (d, 2H), 7.93 (dd, 4H), 7.00 (d, 2H), 4.45 (q, 2H), 1.45 (t, 3H).

*Methyl 4-[[4-(alkanoyloxy)phenyl]diazenyl]benzoates (3a).*

Compound (2a) (0.06 mmol), appropriate carboxylic acid (0.08 mmol), (0.06 mmol) DCC and a pinch DM P were dissolved in dichloromethane. The mixture was stirred at room temperature overnight. Next day the solvent was distilled out and the crude product was purified by column chromatography using dichloromethane as eluent and recrystallized from hexane. Yield: 26–90%.

Purity of the target compounds were tested by elemental analysis (Table I) and NMR spectroscopy, whose results are as follows:

3a-1:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.30 (d, 2H), 3.99 (s, 3H), 2.37 (s, 3H).

3a-2:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.61 (t, 2H), 0.96 (t, 3H).

3a-3:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22(d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.61 (t, 2H), 1.84 (m, 2H), 1.10 (t, 3H).

3a-4:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d, 2H), 7.89

(dd, 4H), 7.19 (d, 2H), 3.88 (s, 3H), 2.53 (t, 2H), 1.69 (q, 2H), 1.40 (m, 2H), 0.91 (t, 3H).

3a-5:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d, 2H), 7.89 (dd, 4H), 7.19 (d, 2H), 3.89 (s, 3H), 2.52 (t, 2H), 1.72 (q, 2H), 1.44–1.27 (m, 4H), 0.87 (t, 3H).

3a-6:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.98 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.62–1.30 (m, 6H), 0.95 (m, 3H).

3a-7:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.98 (s, 3H), 2.62 (t, 2H), 1.81 (q, 2H), 1.51–1.26 (m, 8H), 0.93 (t, 3H).

3a-8:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d, 2H), 7.89 (dd, 4H), 7.19 (d, 2H), 3.89 (s, 3H), 2.52 (t, 2H), 1.71 (q, 2H), 1.39–1.11 (m, 10H), 0.83 (t, 3H).

3a-9:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.50–1.25 (m, 12H), 0.92 (t, 3H).

3a-10:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.50–1.19 (m, 14H), 0.93 (t, 3H).

3a-11:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.52–1.14 (m, 16H), 0.91 (d, 3H).

3a-13:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 4H), 3.99 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.62–1.13 (m, 20H), 0.91 (t, 3H).

3a-15:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.51–1.18 (m, 24H), 0.91 (t, 3H).

3a-16:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.62 (t, 2H), 1.80 (q, 2H), 1.62–1.09 (m, 26H), 0.91 (t, 3H).

3a-17:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 3.99 (s, 3H), 2.62 (t, 2H), 1.81 (q, 2H), 1.62–1.12 (m, 28H), 0.91 (t, 3H).

*Ethyl 4-[[4-(alkanoyloxy)phenyl]diazenyl]benzoates (3b).*

A similar procedure as above was adopted using compound (2b). After solvent evaporation, the crude product was purified by method described above. Yield: 35–75%.

3b-1:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.36 (s, 3H), 1.45 (t, 3H).

3b-2:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.45 (t, 3H), 0.93 (t, 3H).

3b-3:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.84 (m, 2H), 1.45 (t, 3H), 1.09 (t, 3H).

3b-4:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.98 (dd, 4H), 7.28 (d, 2H), 4.44 (q, 2H), 2.62 (t, 2H), 1.79 (q, 2H), 1.55–1.41 (m, 5H), 1.01 (t, 3H).

3b-5:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.45 (t, 3H), 1.81 (q, 2H), 1.49–1.23 (m, 7H), 1.01 (t, 3H).

3b-6:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.98 (dd, 4H), 7.28 (d, 2H), 4.44 (q, 2H), 2.62 (t, 2H), 1.80 (q, 2H), 1.63–1.23 (m, 9H), 0.95 (t, 3H).

3b-7:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.80 (q, 2H), 1.60–1.19 (m, 11H), 0.95 (t, 3H).

3b-8:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.80 (q, 2H), 1.55–1.16 (m, 13H), 0.92 (t, 3H).

3b-9:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.80 (q, 2H), 1.56–1.16 (m, 15H), 0.92 (t, 3H).

3b-10:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.98 (dd, 4H), 7.28 (d, 2H), 4.45 (q, 2H), 2.62 (t, 2H), 1.80 (q, 2H), 1.49–1.18 (m, 17H), 0.92 (t, 3H).

3b-11:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.62 (t, 2H),

1.80 (q, 2H), 1.57–1.20 (m, 19H), 0.91 (t, 3H).

3b-13:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d, 2H), 7.98 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.80 (q, 2H), 1.50–1.23 (m, 23H), 0.91 (t, 3H).

3b-15:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 4.45 (q, 2H), 2.62 (t, 2H), 1.80 (q, 2H), 1.51–1.24 (m, 27H), 0.91 (t, 3H).

3b-16:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.80 (q, 2H), 1.49–1.24 (m, 29H), 0.91 (t, 3H).

3b-17:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.1 (d, 2H), 7.99 (dd, 4H), 7.29 (d, 2H), 4.44 (q, 2H), 2.61 (t, 2H), 1.80 (q, 2H), 1.50–1.24 (m, 31H), 0.91 (t, 3H).

TABLE I

Elemental analysis of methyl (a) and ethyl (b) alkyl 4-[[4-(alkanoyloxy)phenyl]diazenyl]benzoates.

	Calculated			Found				$\Delta = \text{found} - \text{calculated}$		
	N [%]	C [%]	H [%]	N [%]	C [%]	H [%]	O [%]	$\Delta N$ [%]	$\Delta C$ [%]	$\Delta H$ [%]
3a-1	9.307	64.31	4.633	9.39	64.42	4.73	21.45	0.08	0.11	0.10
3a-2	8.942	65.09	5.273	8.97	65.38	5.16	20.49	0.03	0.29	-0.11
3a-3	8.542	66.30	5.474	8.58	66.25	5.56	19.61	0.04	-0.05	0.09
3a-4	8.208	66.89	5.674	8.23	67.05	5.92	18.80	0.02	0.16	0.25
3a-5	7.716	67.84	6.003	7.90	67.78	6.26	18.06	0.18	-0.06	0.26
3a-6	7.599	68.29	6.467	7.60	68.46	6.57	17.37	0.00	0.17	0.10
3a-7	7.216	68.82	6.990	7.32	69.09	6.85	16.73	0.10	0.28	-0.14
3a-8	7.054	69.45	7.359	7.07	69.67	7.12	16.14	0.02	0.22	-0.24
3a-9	6.701	70.39	7.147	6.82	70.22	7.37	15.59	0.12	-0.17	0.22
3a-10	6.643	70.61	7.672	6.60	70.73	7.60	15.07	-0.04	0.12	-0.07
3a-11	6.270	71.01	7.830	6.39	71.21	7.81	14.59	0.12	0.20	-0.02
3a-13	5.959	72.09	8.260	6.00	72.07	8.21	13.72	0.04	-0.02	-0.05
3a-15	5.564	72.96	8.681	5.66	72.84	8.56	12.94	0.10	-0.11	-0.12
3a-16	5.352	73.11	8.456	5.51	73.19	8.72	12.58	0.16	0.08	0.26
3a-17	5.232	73.21	8.702	5.36	73.53	8.87	12.24	0.13	0.32	0.17
3b-1	8.938	65.33	5.147	8.97	65.38	5.16	20.49	0.03	0.05	0.01
3b-2	8.609	66.19	5.565	8.58	66.25	5.56	19.61	-0.03	0.06	0.00
3b-3	8.205	66.87	5.773	8.23	67.05	5.92	18.8	0.03	0.18	0.15
3b-4	7.875	67.62	6.489	7.90	67.78	6.26	18.06	0.03	0.16	-0.23
3b-5	7.567	68.30	6.510	7.60	68.46	6.57	17.37	0.03	0.16	0.06
3b-6	7.271	68.86	7.113	7.32	69.09	6.85	16.73	0.05	0.23	-0.26
3b-7	7.016	69.59	6.910	7.07	69.67	7.12	16.14	0.05	0.08	0.21
3b-8	6.761	70.06	7.623	6.82	70.22	7.37	15.57	0.06	0.16	-0.25
3b-9	6.540	70.58	7.903	6.60	70.73	7.60	15.07	0.06	0.15	-0.30
3b-10	6.250	71.04	7.498	6.39	71.21	7.81	14.59	0.14	0.17	0.31
3b-11	6.147	71.74	7.886	6.19	71.65	8.02	14.14	0.04	-0.09	0.13
3b-13	5.807	72.39	8.488	5.83	72.47	8.39	13.13	0.02	0.08	-0.10
3b-15	5.398	73.20	8.633	5.51	73.19	8.72	12.58	0.11	-0.01	0.09
3b-16	5.232	73.82	8.807	5.36	73.53	8.87	12.24	0.13	-0.28	0.06
3b-17	5.140	74.02	9.094	5.22	73.84	9.01	11.92	0.08	-0.18	-0.08

### 3. Results and discussion

All phase transitions parameters were investigated by two complementary methods, DSC calorimetry and optical polarizing microscopy (POM) with its quantitative version, TO A [16]. All detected phase transition tem-

peratures and their enthalpies are presented in Table II. Both used methods gave the same phase transition temperatures. Typical examples of such measurements are presented in Fig. 2.

TABLE II

Phase transition temperatures (in °C) and enthalpies (in kJ mol<sup>-1</sup>, in square parenthesis) of methyl and ethyl 4-[[4-(alkanoyloxy)phenyl]diazenyl]benzoates.

Compound	Cr(II)		Cr(I)	Melting	Crystallization	SmA		N		Iso
3a-1			•	154.3 [30.25]	150.4 [21.21]					•
3a-2			•	133.7 [37.03]	128.8 [28.49]					•
3a-3			•	125.6 [28.77]	121.5 [28.48]			•	128.7 [0.52]	•
3a-4			•	117.0 [31.89]	112.1 [30.56]					•
3a-5			•	117.8 [33.28]	112.0 [30.60]			•	(115.0) [0.55]	•
3a-6			•	114.6 [35.37]	111.0 [33.17]			•	(113.4) [0.78]	•
3a-7			•	112.4 [38.44]	111.4 [35.46]			•	(116.5) [0.93]	•
3a-8			•	113.7 [39.47]	111.0 [37.21]			•	(113.7) [0.90]	•
3a-9			•	117.1 [42.03] <sup>b</sup>	112.1 [37.88]			•	(115.7) [0.67]	•
3a-10			•	118.6 [37.49]	112.5 [40.92*]			•	(113.6) [40.92*]	•
3a-11			•	119.9 [39.27]	112.8 [40.57]			•	(113.2) [0.90]	•
3a-13			•	115.0 [51.49]	113.4 [60.40]					•
3a-15			•	116.7 [69.49]	112.8 [67.24]					•
3a-16			•	117.8 [74.29]	113.7 [74.94]					•
3a-17			•	116.6 [74.35]	113.9 [72.15]					•
3b-1			•	115.4 [29.79]	106.9 [29.15]					•
3b-2	•	96.7 [15.87]	•	105.9 [27.32]	98.6 [8.53]					•
3b-3	•	77.8 [28.66*]	•	96.6 [30.31]	78.6 [28.66*]			•	(83.9) [0.26]	•
3b-4			•	80.1 [37.21] <sup>b</sup>	69.5 <sup>a</sup> [26.06*]	•	(70.6) [26.06*]	•	(73.5) [0.20]	•
3b-5			•	79.7 [27.13]	63.3 [18.65]	•	(68.2) [3.38]	•	83.7 [0.44]	•
3b-6			•	83.0 [32.87]	69.2 [23.49]	•	(71.8) [4.01]	•	(79.4) [0.47]	•
3b-7			•	86.6 [34.95]	68.9 [22.38]	•	(79.4) [4.05]	•	(86.3) [0.74]	•
3b-8	•	85.0 [**]	•	83.0 [38.20] <sup>b</sup>	72.7 [38.65]	•	(84.1) [6.01*]	•	86.6 [6.01*]	•
3b-9			•	92.0 [50.06]	84.7 [32.71]	•	(87.3) [5.75*]	•	(90.7) [5.75*]	•
3b-10			•	85.1 [46.18] <sup>b</sup>	74.4 [31.64]	•	90.5 [8.36]			•
3b-11			•	88.9 [34.80]	74.8 [29.06]	•	93.0 [8.98]			•
3b-13			•	94.0 [54.70]	79.6 [39.49]	•	(92.2) [9.56]			•
3b-15			•	97.0 [63.50]	86.0 [51.29]	•	(91.6) [10.08]			•
3b-16			•	98.9 [68.85] <sup>b</sup>	89.1 [68.93*]	•	(90.7) [68.93*]			•
3b-17			•	98.7 [68.78]	90.8 [69.63]					•

<sup>a</sup> Temperature estimated due to overlapping of peaks.

<sup>b</sup> Enthalpy approximate because of overlapping of peaks of various phase transitions.

\* Given a common heat of two phase transformation.

\*\* Heat cannot be determined due to the complex sequence of exothermic and endothermic processes.

In the cooling mode both methods show the presence of two mesophases and the texture observations (Fig. 3a and b) indicates that these two mesophases are: nematic and smectic A. Nematic mesophase is monotropic and smectic A enantiotropic. In TO measurements light intensity in the nematic phase is the same as in isotropic phase. Such results are typical for homeotropic sample orientation. Usually in the phase transition point observed light intensity is very low. That is connected with the increasing anisotropic character of the phase and its homeotropisation. In the heating mode there is observed unexpected phenomenon. In the cooling mode it grows up from smectic A a new thermodynamically unstable phase, the solid one (Cr(I)). This phase (Cr(I)) in the heating process melts in 83 °C to the nematic mesophase,

which is shown in Fig. 3c. Probably Cr(I) at first is melts to smectic A. But both mesophases temperature ranges are very narrow and the melting process with significant enthalpy covers smectic A creation. Only nematic phase is able to observe during the melting. An unexpected result was the new crystal phase (Cr(II)) that grows up in the heating mode at the 85 °C. This process continues further in the isotropic phase and next Cr(II) melts nearly 90 °C. Growing up of Cr(II) in heating mode is shown in Fig. 3d. Transformation to Cr(II) we can speed up by stop heating in 86 °C. Such process of creation Cr(II) is untypical and very seriously complicates proper description of phase situation.

By using two complementary methods DSC and TO we were able to search mesogenic properties of both homol-

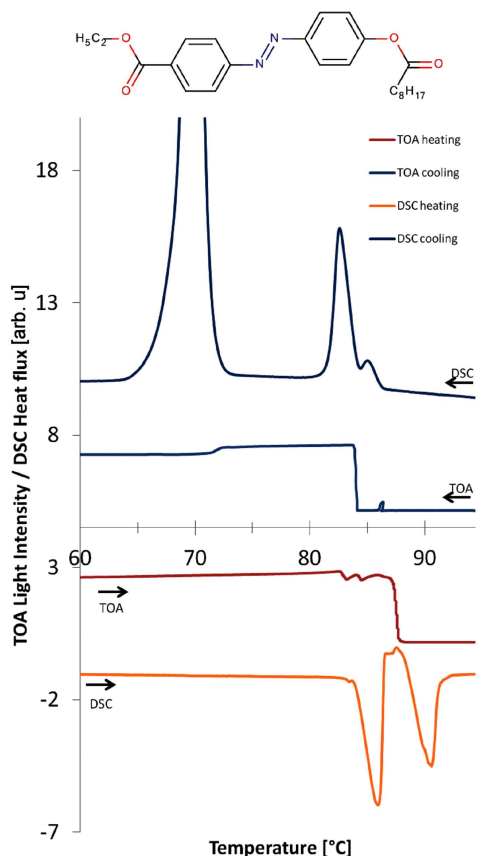


Fig. 2. DSC and TO scans of ethyl 4-[[4-(nonanoyloxy)phenyl]diazanyl]benzoate (3b-8).

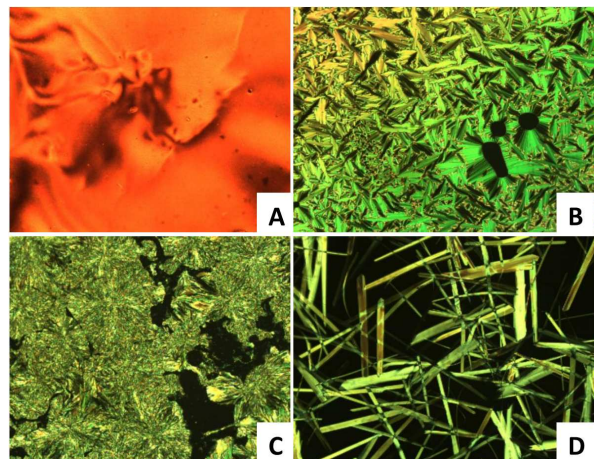


Fig. 3. Textures of ethyl 4-[[4-(nonanoyloxy)phenyl]diazanyl]benzoate (3b-8) seen by polarizing microscopy. (A) Nematic phase. (B) S<sub>m</sub>A phase. (C) The solid phase (Cr(I)) formed during the cooling smectic A. (D) Crystals (Cr(II)) growing up during the heating of 3b-8 after N-Iso phase transition.

ogous series. In the first series 3a-n, methyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates, we observe only nematic phase. Influence of alkyl chain length on the phase transition temperatures is shown in Fig. 4. We observe relatively high melting temperatures for the first three derivatives, which decrease from 154.3°C (ethyl derivative) to 125.6°C (butyl derivative). Remaining derivatives have typical melting temperatures values in the range from 112°C to 120°C. In this series nematic phase in majority case is monotropic. Only butyl and octyl derivatives are enantiotropic. Clear even-odd effect of isotropisation temperature is visible with decrease of its average values along with extending chain length. It is exceptional butyl derivative with highest temperature of isotropisation, 128°C. The next one, pentyl derivative, is non-mesogenic. Low isotropisation temperature and high melting and freezing temperatures are the causes of our observations. The same reason is responsible for the non-mesogeneity of the last three derivatives, 3a-13, 3a-15 and 3a-17.

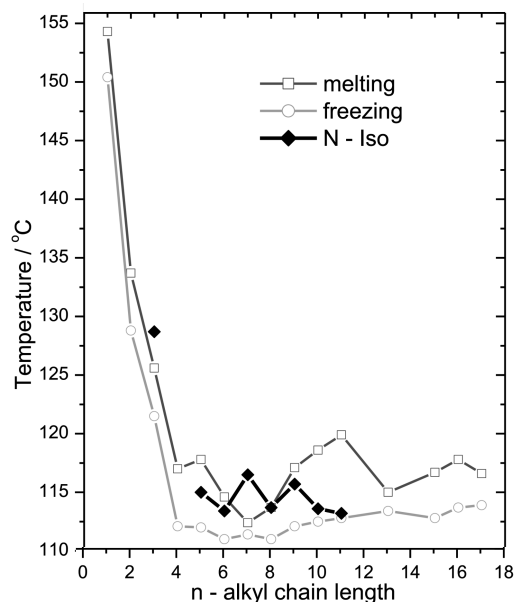


Fig. 4. Phase transition temperatures of (3a-n) series, methyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates.

In the second investigated series 3b-n, ethyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates, mesomorphism is richer. We observed two kinds of mesophases: nematic and smectic A, which indicate the textures observations (Fig. 3a and b).

Influence of the alkyl chain length on phase transition temperatures of the second homologous series 3b-n, ethyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates, has been presented in Fig. 5. Just as in the 3a-n series the first three derivatives have significantly higher melting temperature than others and they are as follows 115°C, 107°C and 97°C. From hexyl derivative melting temperature starts to increase. Decrease of melting tem-

perature is non-typical for undecyl derivative about 8 °C and simultaneously nematic phase disappears. Iso small value of melting hysteresis is very characteristic for decyl derivative. In this series nematic phase is observed from butyl to decyl derivatives with very distinct even-odd effect of isotropisation temperature. From pentyl to heptadecyl derivatives there was observed extra smectic mesophase. The presence of this mesophase in octadecyl derivative at very fast cooling is also possible.

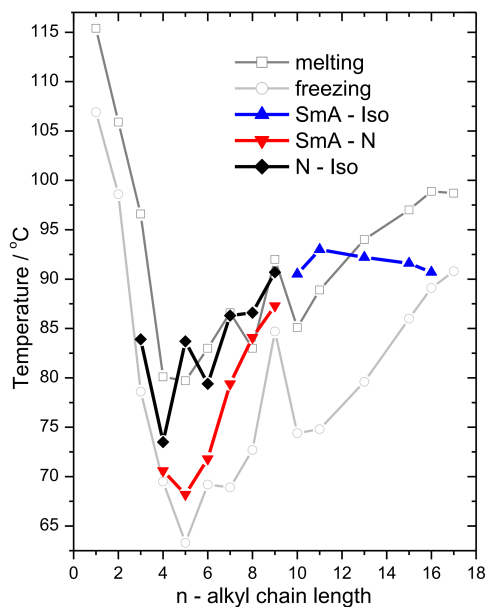


Fig. 5. Phase transition temperatures of 3b-n series, ethyl 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoates.

From this series four derivatives were also investigated by Chinese group from Taiwan [12–14]. The most controversial is the decyl derivative in comparison with our results. They report that only one mesophase SmB is present. Furthermore, they did not observe either crystallization or glass transition. Our DSC and TO results are presented in Fig. 6. Differential scanning calorimetry measurements in the cooling mode of this substance showed two peaks, including one complex, which correspond to three transformations: from isotropic phase to the nematic, N–SmA and crystallization (Fig. 6). If mesophases have a very narrow range and appear after the beginning of the crystallization process. Such situations are visible in Fig. 7c and d, where among growing up crystals there are areas with typical textures of nematic (Fig. 7c) and smectic A (Fig. 7d). The temperature of melting is a proof of monotropic character of observed mesophases. We think that the Lai et al. results have been misinterpreted, but properly measured. It is possible that monotropic mesophases are invisible, especially when low rate of cooling is used. According to their interpretation the enthalpy of isotropic to smectic B phase transition has too high value, corresponding rather to crystallization process. Furthermore, the shape

of the XRD spectra shown in their work is more appropriate for the crystalline phase, not for liquid-crystalline. Moreover it is very unusual that in the homologous series only one derivative has one mesophase SmB and the neighbor derivatives have nematic and smectic A.

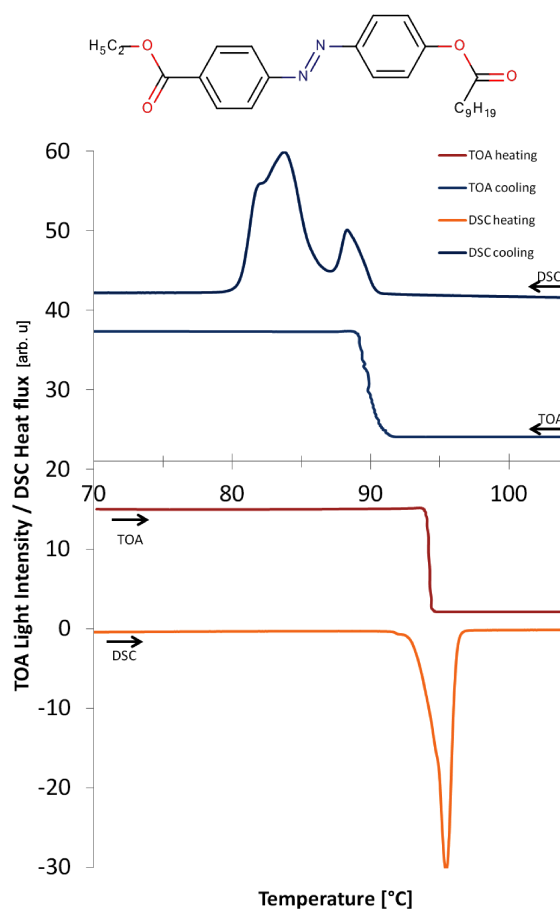


Fig. 6. DSC and TO scans of ethyl 4-[[4-(decanoyloxy)phenyl]diazanyl]benzoate.

Another interesting phenomenon observed in this series is the solid phase polymorphism. The most significant Cr–Cr phase transition is observed in the propyl (3b-2), butyl (3b-3) and nonyl (3b-8) derivatives. Relatively high entropy value of this phase transition can be connected with the orientational disordered crystal (ODIC) character of the high-temperature phase.

In both homologous series only two types of mesophases are observed: nematic and smectic A. Very interesting are entropic effects. There were taken into account only these phase transitions for which the enthalpy was possible exactly to measure. Such conditions fulfilled only six derivatives with both mesophases, five with smectic A only and nine with nematic. Because of similarity of the structure we can compare the entropy of liquid crystalline phase transition. These results are presented in Fig. 8. The phase transition nematic-isotropic has the entropy value nearly constant with the average

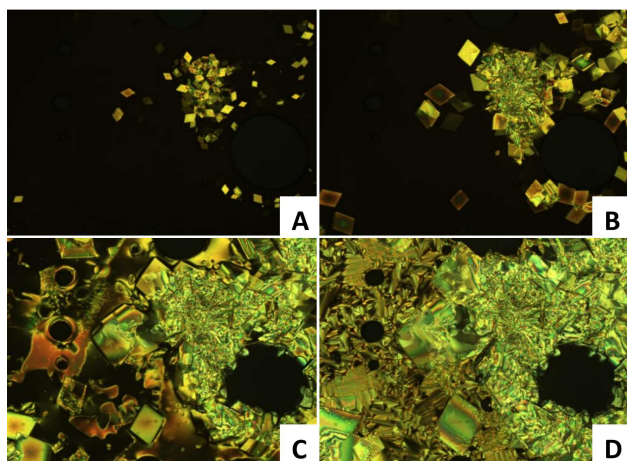


Fig. 7. Textures of ethyl 4-[[4-(decanoyloxy)phenyl]diazanyl]benzoate (3b-9) observed by polarizing microscopy. (A) Beginning of the crystallization process. (B) Further stage of the crystallization process. (C) Nematic phase with the partial process of crystallization. (D) SmA phase with the partial process of crystallization.

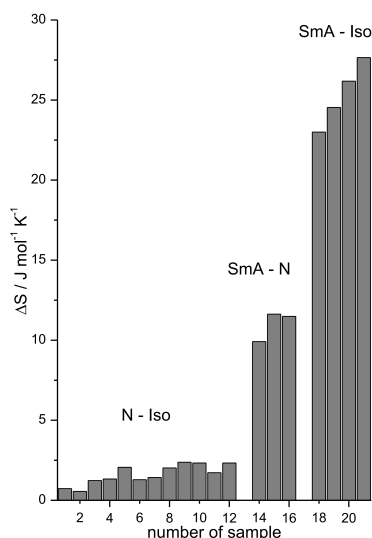


Fig. 8. Entropies of the investigated liquid-crystalline phase transitions.

value  $1.62 \text{ J K}^{-1} \text{ mol}^{-1}$ . For the nematic–smectic A this value is  $11.01 \text{ J K}^{-1} \text{ mol}^{-1}$  and for smectic A–isotropic  $25.34 \text{ J K}^{-1} \text{ mol}^{-1}$ . These values are characteristic for these phase transition and can be helpful in interpretation of the unknown liquid-crystalline phase transitions. Unexpected is the result of entropic non-additivity:

$$\Delta S_{\text{SmA-Iso}} > \Delta S_{\text{SmA-N}} + \Delta S_{\text{N-Iso}}$$

#### 4. Conclusions

In this paper there are presented synthesis and investigations of liquid crystalline properties with the help DSC

calorimetry and polarizing microscopy two homologous series of 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoic acid esters. For the methyl ester series very poor liquid crystalline polymorphism was detected. Only nematic mesophase, mainly monotropic, was found. It is probably connected with relatively very high melting temperatures. For the second series richer polymorphism has been detected with the presence of nematic and smectic A mesophases. Very characteristic even–odd effect of clearing temperature was found. From received in this paper results we can conclude that this group of compounds, 4-[[4-(alkanoyloxy)phenyl]diazanyl]benzoic acid alkyl esters, are rather poorly mesomorphic. Even for the tetradecyl derivative of ethyl esters series only smectic A mesophase was observed. But because their *cis-trans* isomerization effect, liquid-crystalline properties and relatively low phase transition temperatures they can be useful as the photorefractive materials in modern optics.

#### References

- [1] T. Rotarski, *Ber. Deut. Chem. Ges.* **36**, 3158 (1903).
- [2] A. Bogojawlensky, N. Winogradow, *Z. Phys. Chem.* **64**, 229 (1908).
- [3] F. Dreyer, T. Rotarski, *Z. Phys. Chem.* **54**, 353 (1906).
- [4] D. Vorländer, *Ber. Deut. Chem. Ges.* **71**, 1688 (1938).
- [5] V. Vill, *Liq Cryst. 5.2*, LCI Publisher GmbH, Hamburg 2013.
- [6] T. Ikeda, T. Sasaki, K. Ichimura, *Nature* **361**, 428 (1993).
- [7] T. Ikeda, *J. Mater. Chem.* **13**, 2037 (2003).
- [8] J. Mysliwiec, M. Czajkowski, S. Bartkiewicz, K. Zygadlo, Z. Galewski, B. Sakhraoui, *J. Appl. Phys.* **110**, 113104 (2011).
- [9] A. Sobolewska, J. Zawada, S. Bartkiewicz, Z. Galewski, *J. Phys. Chem. C* **117**, 10051 (2013).
- [10] K. Bergt, Ph.D. Thesis, Halle 1925.
- [11] L.E. Knaak, H.M. Rosenberg, M.P. Servé, *Mol. Cryst. Liq. Cryst.* **17**, 171 (1972).
- [12] L.L. Lai, F.Y. Su, K.C. Zhan, Y.L. Cai, Y.H. Liu, Y. Wang, *J. Chin. Chem. Soc. (Taipei)* **54**, 197 (2007).
- [13] L.L. Lai, F.Y. Su, C.H. Hung, *Liq. Cryst.* **31**, 773 (2004).
- [14] L.-L. Lai, F.-Y. Su, Y.-J. Lin, C.-H. Ho, E. Wang, C.-H. Hung, Y.-H. Liu, Y. Wang, *Helv. Chim. Acta* **85**, 1517 (2002).
- [15] C.L. Hillemann, G.R. Van Hecke, S.R. Peak, J.B. Winther, M.A. Rudat, D.A. Kalman, M.L. White, *J. Phys. Chem.* **79**, 1566 (1975).
- [16] Z. Galewski, H.J. Coles, *J. Mol. Liq.* **79**, 77 (1999).